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USE OF COLEMANITE IN GLASS FIBER PRODUCTION

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The possibility of replacing boric acid with colemanite in the mix composition of glass is assessed for type E borosilicate glass. The processes occurring during glass making at the silicate- and glass-forming stages are examined. The effect of colemanite on these processes is studied.

Key words: borosilicate glass, mix, boric acid, colemanite, silicate and glass formation, fining, glass fiber.

The production of glass fiber and the expansion of the applications of glass-fiber materials possessing special properties which are not characteristic of natural materials have accelerated in recent years.

Glass fiber made of type-E calcium – aluminum – borosilicate glass, containing less than 1%³ alkali-metal oxides has been most widely adopted throughout the world [1]. It is characterized by the high chemical resistance to water, good dielectric properties (resistivity $10^{12} \Omega \cdot \text{m}$), quite high strength (to 3300 MPa), and low CLTE ($60 \times 10^{-7} \text{ K}^{-1}$).

However, type E glass has a number of technological drawbacks. The serious one is that this glass contains a volatile component — boron oxide, which is introduced into the mix via boric acid. In this case the B_2O_3 losses during glassmaking are about 15%, which often causes a breakdown of the chemical uniformity of the glass, product quality degradation, and contamination of the environment. In addition, boric acid is in short supply and expensive [1, 2].

These problems can be partially solved by using colemanite as an alternative to boric acid as a source of boron oxide in making borosilicate glass, since the volatility of boron anhydride largely depends on the forms and methods used to introduce the oxide into the mix as well as on the degree of binding of the oxide in various chemical compounds at different stages of the silicate and glass formation processes during glass synthesis.

Colemanite is a white or yellowish sedimentary rock of chemogenic origin. It consists mainly of colemanite mineral $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot \text{H}_2\text{O}$ with calcite CaCO_3 impurities, character-

ized by Moohs hardness 4.0 – 4.5 and high density 2402 – 2600 kg/m^3 .

The experiments were performed using colemanite from the Eti Mine Works G.M. Company (Turkey). Its chemical composition is as follows (%): 5.66 SiO_2 , 36.54 B_2O_3 , 0.35 Al_2O_3 , 23.49 CaO , 2.61 MgO , 0.30 Na_2O , 0.70 Fe_2O_3 , and 30.98 other.

Differential – thermal analysis of colemanite (Fig. 1) showed that the initial material undergoes a series of transformations when heated. For example, a two-step endothermic effect with minima at 360 and 380°C is observed in the temperature interval 310 – 420°C. The total mass losses are 23%. A further increase of temperature is accompanied by the appearance of an exothermic effect peaking at 710°C.

X-ray phase analysis of the initial colemanite as well as colemanite treated at 400 and 800°C was performed to explain the nature of the processes indicated above. It was established that complete destruction of the crystal structure of colemanite occurs during heat-treatment at 360 and 380°C. This was confirmed by DTA data. In addition, the colemanite transitions into an amorphous state with the initial amount of CaCO_3 being conserved. The formation of a crystal com-

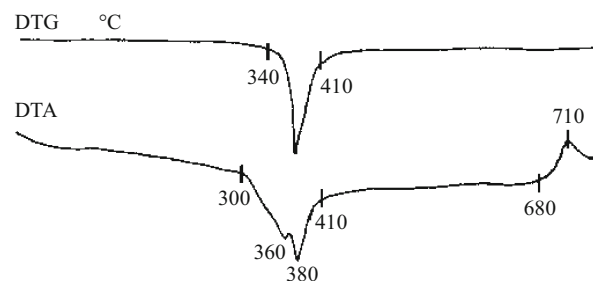


Fig. 1. Differential – thermal analysis of colemanite.

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³ Here and below — content by weight.

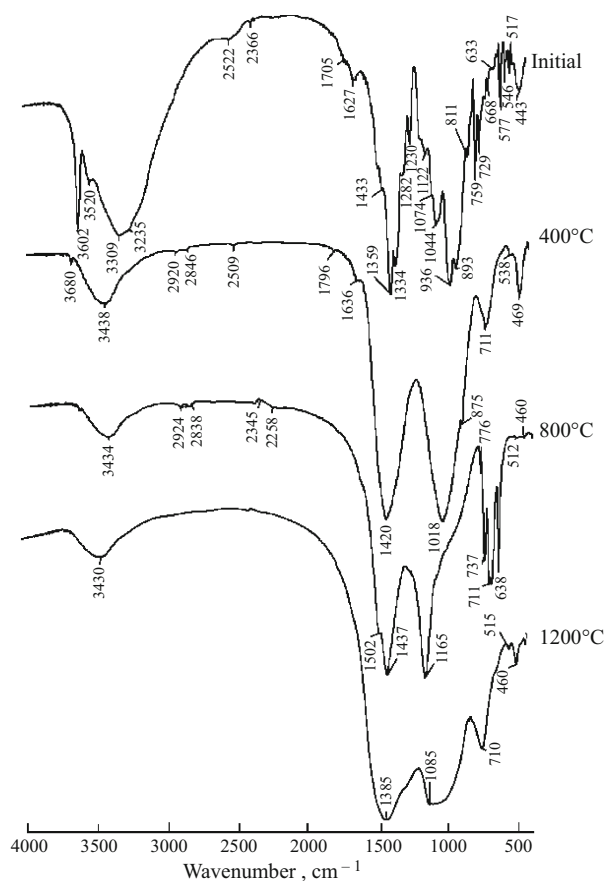


Fig. 2. IR spectra of the colemanite in its initial state and heat-treated at different temperatures.

pound — calcium borate — is recorded at 710°C; this explains the corresponding exoeffect on the thermogram.

The IR spectra of the initial and heat-treated colemanite (Fig. 2) make it possible to supplement the information obtained by x-ray phase and differential — thermal analyses.

Strong absorption bands in the interval 3650 – 3200 cm^{-1} (symmetric and asymmetric stretching vibrations of OH groups) and in the region 1500 – 400 cm^{-1} (stretching and deformation vibrations of the B – O bonds) are observed in the IR spectrum of the initial colemanite. The presence of comparatively narrow bands at 3605 and 3520 cm^{-1} indicates that relatively free OH groups are present in the structure of colemanite. The strong wide band in the region 3310 – 3235 cm^{-1} is due to the stretching vibrations of OH groups associated with quite strong hydrogen bonds. The absorption band with a minimum at 1627 cm^{-1} corresponds to deformational vibrations of water molecules. The large number of absorption bands in the region of the stretching and deformational vibrations of the B – O bonds (1400 – 400 cm^{-1}) is due to the low symmetry of the crystal lattice of colemanite (monoclinic system) as well as the presence of boron in different (trigonal and tetragonal) coordinations.

In addition, absorption bands at 1445, 1433, 875, and 711 cm^{-1} , corresponding to stretching and deformation vi-

brations of the C – O bands in the anion CO_3^{2-} , are observed in the IR spectrum. This agrees with the XPA data on the presence of calcite CaCO_3 in the initial colemanite. Absorption bands corresponding to the stretching and deformation vibrations of B – O bonds appear in the interval 1500 – 1400 cm^{-1} . The large number of bands in this region is due to the low symmetry of the crystal lattice of colemanite (monoclinic system) as well as the presence of boron in the trigonal and tetragonal coordinations.

The absorption spectrum of colemanite which has undergone heat-treatment at 400°C changes substantially with respect to the number and position of bands. The absorption bands broaden substantially and become structureless, which is characteristic for an amorphous structure. Groupings containing O – H groups as well as trigonally and tetragonally coordinated boron atoms decompose, thereby giving rise to the appearance of a polyborate amorphous phase. The absorption bands corresponding to the stretching (asymmetric and symmetric) vibrations of the B – O bands shift to the high-frequency region as compared with the vibrations of the B – O bands in the initial colemanite. The bands due to the stretching vibrations of the anion CO_3^{2-} overlap with the strong due to B – O band stretching vibrations of the anion in the interval 1600 – 1300 cm^{-1} .

A further increase of the temperature to 800°C results in the formation of crystalline calcium polyborate – metaborate. The absorption bands at 1420 and 1010 cm^{-1} become narrower, their maxima shift to high frequencies — 1427 (shoulder at 1500 cm^{-1}) and 1165 cm^{-1} , respectively.

The absorption spectrum of colemanite which has been heat-treated at 1200°C and consists of a transparent glassy material possesses principal absorption bands at 3430, 1385, 710, and 460 cm^{-1} , attesting to the existence of predominately $[\text{BO}_4]$ groups, which will be completely incorporated into the structure of the glassy phase network when glaze coatings are obtained.

The possibilities of using colemanite in glass-fiber production were investigated for type E glass with commercial composition, intended for the production of a continuous glass fiber using a single-stage technology. The H_3BO_3 in the mix composition of the glass was replaced with $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot \text{H}_2\text{O}$ in the following ratios: composition No. 1 — 0 : 100, No. 2 — 50 : 50, No. 3 — 100 : 0. Boric acid was introduced in the amount 15% into the mix with a correction for the evaporation of boric acid. Evaporation was neglected for colemanite.

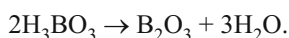
The raw material components comminuted to particle size less than 400 μm were used to make the mix.

The glass was made at temperature $1500 \pm 10^\circ\text{C}$ in a periodic-action gas-flame laboratory furnace. Additional heat-treatment of the mix with soaking at the maximum temperature for 1 h was performed at 500, 700, 900, and 1050°C to study silicate and glass formation processes. Optical, x-ray diffraction, and thermal methods were used for the investiga-

tions. A visual evaluation of the products of heat-treatment of the mix is presented in Table 1.

Differential – thermal analysis of the composition No. 1 (Fig. 3) showed that four endoeffects accompanied by losses of mass of the sample are observed in the temperature interval 60 – 900°C. No explicit endoeffects indicating the silicate-formation reactions in the mix were observed. At the same time XPA of mix (Fig. 4) heat-treated at 700, 900, and 1100°C shows clearly that such processes proceed quite actively.

The first reactions in the mix with the participation of boric acid were observed in the temperature interval 60 – 215°C and are related with losses of H_3BO_3 chemically bound with water:



According to [3], partial decomposition of the molecules of orthoboric acid H_3BO_3 ($B_2O_3 \cdot 3H_2O$) with water being released and transformation into metaboric acid HBO_2 ($B_2O_3 \cdot H_2O$) occur in the indicated temperature range. The released water in the form of hydroxyl acts as a mineralizer and has a large effect on the course of all subsequent glass-formation processes. It lowers the melting temperature and decreases the viscosity of the liquid phase. A liquid phase is observed to appear at 158°C as a result of the formation of a eutectic between H_3BO_3 and HBO_2 . During subsequent heating the amount of this phase gradually increases as a result of melting of H_3BO_3 , which is observed at 170°C, and HBO_2 at 176°C, as well as several subsequently forming eutectics in which B_2O_3 participates [3].

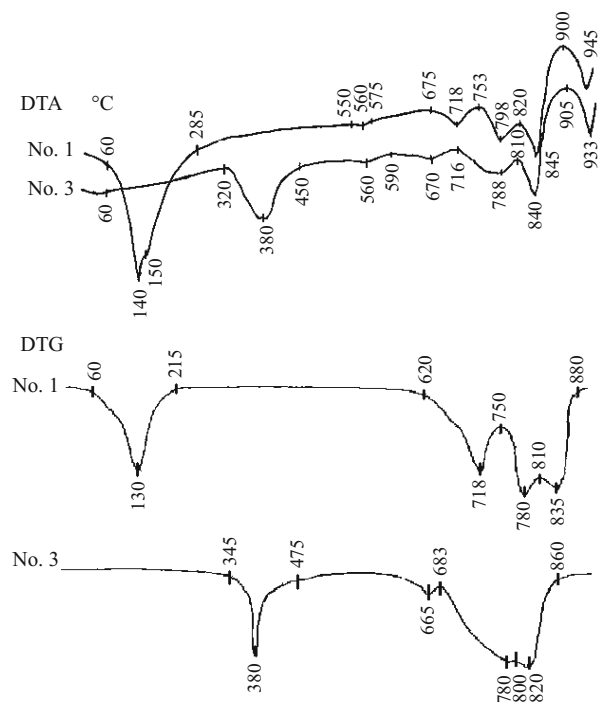


Fig. 3. DTA curves of borosilicate glass batch based on boron hydroxide (No. 1) and colemanite (No. 3).

Under the influence of B_2O_3 , which melts at 450 – 470°C, sintering of the mix and silicate-formation reactions occur (see Table 1).

Calcium borates and calcium and magnesium borates start to form together with decarbonization processes. According to DTA, the crystal structure of magnesium carbonate, which is a component of dolomite, breaks down at 620 –

TABLE 1.

Temperature, °C		Composition	
	No. 1	No. 2	No. 3
500	Product of heat-treatment was extracted in the form of sinter from the crucible. A small part, about 15%, was in a free-flowing form	Weak sintering of grains in the mix. Free-flowing part comprise 15 – 20%	Sintering not observed. Mix increased in volume by 10 – 20%
700	A dense sintered mass was formed	Degree of sintering of the grains of mix increased. The free-flowing part was 5 – 10%	Weak sintering of mix grains
900	Product of heat-treatment represented by a dense sintered mass	Dense sintered mass formed	Dense sintered mass formed. Nonuniform distribution of pores observed on the surface of the sinter
1100	Product is partially fused; glass sheen has appeared	Product almost completely melted	Nonuniform opaque melt saturated with gases formed
1500	Glass fully made and fined. Number of bubbles per 1 cm ² was (%): 1.7 mm — 10, 0.5 – 0.7 mm — 10, 0.1 mm — 80	Glass adequately made and fined. Number of bubbles per 1 cm ² as (%): 1. 3 mm and larger — 10, 0.5 – 0.7 mm — 10, 0.3 mm — 20, 0.1 mm and smaller — 60	Glass adequately made and fined. Number of bubbles per 1 cm ² as (%): 1.3 – 1.0 mm — 10, 0.5 – 0.7 mm — 10, 0.4 – 0.3 mm — 30, 0.1 – 0.2 mm — 50

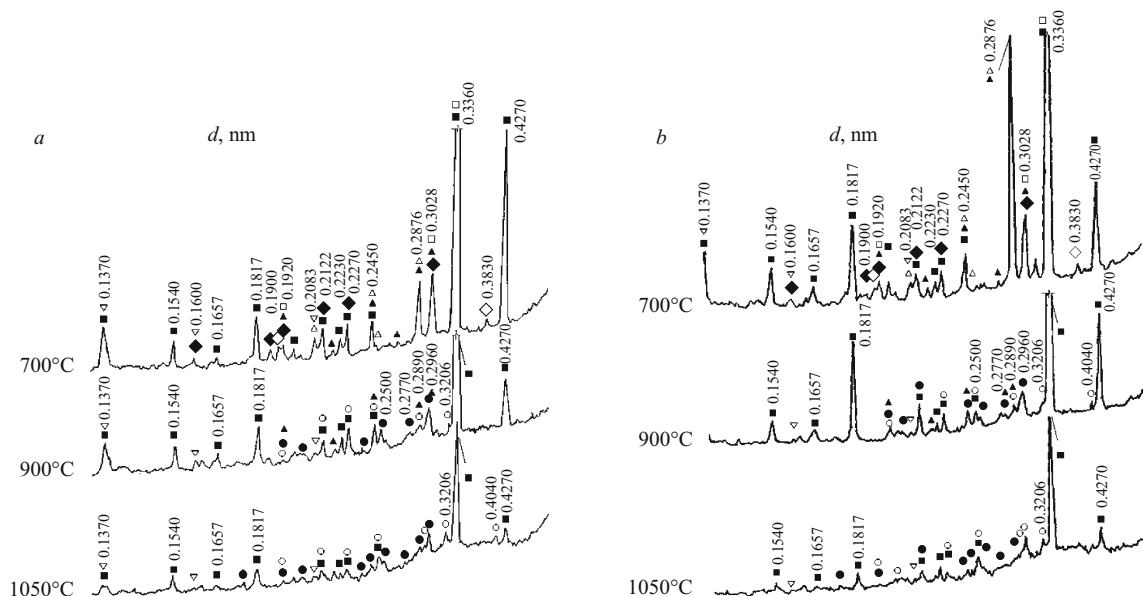
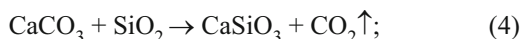
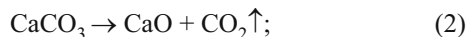
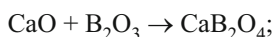
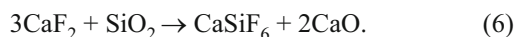


Fig. 4. XPA of borosilicate glass mix made with the boric acid (*a*) and colemanite (*b*): ■ SiO_2 ; ◇ CaCO_3 ; △ MgSiO_3 ; ▲ CaSiO_3 ; □ CaB_2O_4 ; <◇> CaSiF_6 ; ○ $\text{Ca}[\text{Si}_2\text{B}_2\text{O}_8]$; ● $\text{Ca}[\text{Si}_2\text{Al}_2\text{O}_8]$; ▼ Al_2O_3 .

750°C. Calcium carbonate breaks down at 750–880°C. Decarbonization of CaCO_3 , which is a component of dolomite, occurs especially actively at 780°C and that of chalk at 835°C.

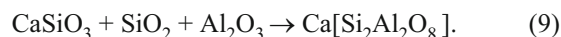
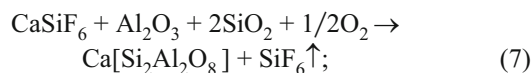


Calcium silicate CaSiO_3 and magnesium silicate MgSiO_3 are recorded in the x-ray diffraction pattern of the mix heat-treated at 700°C, and quartz SiO_2 , corundum Al_2O_3 , and calcium carbonate CaCO_3 are seen to be present. Calcium silicon fluoride CaSiF_6 is found. The latter compound is formed when silicon oxide interacts with calcium fluoride present in the mix:



X-ray phase analysis showed anortite $\text{Ca}[\text{Si}_2\text{Al}_2\text{O}_8]$ and calcium borosilicate — danburite $\text{Ca}[\text{Si}_2\text{B}_2\text{O}_8]$ to be present in embryos at 900 and 1050°C. The relative intensity of the diffraction peaks, which indirectly attest to the amount of the indicated phases in the mix, show that calcium borosilicate

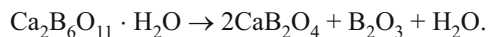
forms first. Its content in the mix is highest at 900°C. The highest amount of anortite is observed at 1100°C:



Silica and aluminum oxide practically do not interact with boron anhydride when the mix is heat-treated to 700°C and they are not dissolved by borate glass. The activity of SiO_2 and Al_2O_3 interacting with borates and their solubility in the liquid phase start to increase sharply at 800°C. The eutectic melts which form in the temperature interval 700–1100°C between calcium metaborate and calcium silicates, anortite, and danburite can have a positive effect on this process. It is precisely the formation of compounds between the calcium, boron, silicon, and aluminum oxides that promotes more active dissolution of refractory components of the system (SiO_2 and Al_2O_3) in the melt and gradual transformation of a heterogeneous substance into a homogeneous melt.

The first processes in a mix based on colemanite (composition No. 3) are related with the dehydration of $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot \text{H}_2\text{O}$. A two-step endoeffect accompanied by 2.8 wt.% loss of the sample is observed in the thermogram in the temperature interval 345–450°C. Boron anhydride and an amorphous substance are formed in the course of the reaction; the amor-

phous substance subsequently crystallizes in the form of calcium metaborate:



Subsequent processes in the mix proceed according to the reactions (1) – (9). In the temperature interval 400 – 500°C, a mix based on colemanite increases in volume by 10 – 20% and the mix sinters in the interval 700 – 900°C.

The volatility of boron anhydride was determined indirectly by measuring and comparing the physical – chemical properties of glasses synthesized using colemanite and boric acid. As already noted during synthesis of glasses, the mix based on boric acid was composed taking account of the 15% correction for evaporation of boron oxide, and the mix based on colemanite was composed without taking losses into account. Since no differences were observed in the level of the properties (the density of the glasses, the CLTE, the softening onset temperature were determined), the glasses can be assumed to have identical chemical compositions; there is practically no volatility of boron oxide when colemanite is used.

During melting of a mix containing boric acid, boron anhydride already starts to evaporate at 150°C and this process is associated with the removal of H_3BO_3 with the vapor. According to the data of [3], at 500°C up to 6% boric acid evaporates from H_3BO_3 . Evaporation of B_2O_3 from colemanite does not occur under the same conditions — this compound is bound. The subsequent evaporation of boric anhydride during glass formation is closely related to the structure of the silicate melt and the form in which it is found in the course of the silicate and glass formation processes. When colemanite is used, most of the boron oxide is bound in cal-

cium borate and calcium borosilicate, which lowers the losses of the boron anhydride during glassmaking.

In summary, when colemanite is introduced into the mix the glass- and silicate-formation processes in the mix accelerate, glassmaking is greatly facilitated because more boron oxide is drawn into the silicate-formation process than in the case of a mix based on boric acid. The calcium boro- and aluminosilicate formed in the course of the reaction promote more rapid conversion of refractory components of the system into melt. However, during heat treatment at about 500°C a colemanite-based mix increases in volume by 10 – 20% because of dehydration of $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot \text{H}_2\text{O}$. This must be kept in mind during commercial founding of calcium-aluminosilicate glass based on colemanite.

Boron oxide losses during glassmaking are reduced when colemanite is used. In the course of the glass- and silicate-formation processes most of the boron oxide is in a chemically bound state: colemanite → calcium borate → calcium borosilicate. Decreasing the volatility of boron anhydride will make it possible to increase product quality and decrease the harmful effect of B_2O_3 on the ecology as a whole.

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